


FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>220258US0PCT</b>	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <b>10/088530</b>	
INTERNATIONAL APPLICATION NO. <b>PCT/EP00/09627</b>		INTERNATIONAL FILING DATE <b>2 October 2000</b>		PRIORITY DATE CLAIMED <b>2 October 1999</b>	
TITLE OF INVENTION <b>POLYMERIZABLE SOLID ALIPHATIC POLYURETHANES WHICH CONTAIN OLEFINICALLY UNSATURATED DOUBLE BONDS AND WHICH ARE BASED ON LINEAR DIISOCYNATES, AND THEIR USE</b>					
APPLICANT(S) FOR DO/EO/US <b>BRUCHMANN, Bernd et al.</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.</li> <li>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto.</li> <li>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> have been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li>10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> <li>11. <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li>12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> </ol>					
<b>Items 13 to 20 below concern document(s) or information included:</b>					
<ol style="list-style-type: none"> <li>13. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>15. <input type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>16. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>17. <input type="checkbox"/> A substitute specification.</li> <li>18. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li>20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li>21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li>22. <input type="checkbox"/> Certificate of Mailing by Express Mail</li> <li>23. <input checked="" type="checkbox"/> Other items or information: <b>Notice of Priority/Form PTO-1449/Application Data Sheet (3 pages)</b></li> </ol>					

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
10/088530		PCT/EP00/09627		220258US0PCT	
24. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5)) :					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . . \$1040.00					
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . . \$890.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . \$740.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . \$710.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	- 20 =	0	x \$18.00	\$0.00	
Independent claims	- 3 =	0	x \$84.00	\$0.00	
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$890.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$890.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 +				\$130.00	
TOTAL NATIONAL FEE =				\$1,020.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).			<input type="checkbox"/>	\$0.00	
TOTAL FEES ENCLOSED =				\$1,020.00	
				Amount to be refunded	\$
				charged	\$
a.	<input checked="" type="checkbox"/>	A check in the amount of \$1,020.00 to cover the above fees is enclosed.			
b.	<input type="checkbox"/>	Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.			
c.	<input checked="" type="checkbox"/>	The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed.			
d.	<input type="checkbox"/>	Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.			
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
<div style="border: 1px solid black; padding: 10px;"><div>Surinder Sachar Registration No. 34,423  22850</div></div>					
<div>Surinder Sachar SIGNATURE Norman F. Oblon NAME 24,618 REGISTRATION NUMBER April 2 2002 DATE</div>					

APPLICATION DATA SHEET

APPLICATION INFORMATION

Application Type::	REGULAR
Subject Matter::	UTILITY
CD-ROM or CD-R?::	NONE
Title::	POLYMERIZABLE SOLID ALIPHATIC POLYURETHANES WHICH CONTAIN OLEFINICALLY UNSATURATED DOUBLE BONDS AND WHICH ARE BASED ON LINEAR DIISOCYNATES, AND THEIR USE
Attorney Docket Number::	220258US0PCT

INVENTOR INFORMATION

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#### CORRESPONDENCE INFORMATION

Correspondence Customer Number:: 22850

#### REPRESENTATIVE INFORMATION

Representative Customer Number:: 22850

#### DOMESTIC PRIORITY INFORMATION

Application::	Continuity Type::	Parent Application::	Parent Filing Date::
This Application	National Stage of	PCT/EP00/09627	10/02/00

#### FOREIGN PRIORITY INFORMATION

Application Number:	Country::	Filing Date::	Priority Claimed::
199 47 522	Germany	10/02/99	YES

#### ASSIGNMENT INFORMATION

Assignee Name:: BASF Akiengesellschaft  
 City of Mailing Address:: Ludwigshafen

Country of Mailing Address:: GERMANY  
Postal or Zip Code of Mailing Address:: D-67056

10/088530  
Rec'd PCT/PTO 15 AUG 2002

220258US-524-524-0-PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

:

BERND BRUCHMANN ET AL

: ATTN: APPLICATION DIVISION

SERIAL NO: 10/088,530

:

FILED: APRIL 2, 2002

: EXAMINER:

FOR: POLYMERIZABLE SOLID ALIPHATIC  
POLYURETHANES WHICH CONTAIN  
OLEFINICALLY UNSATURATED DOUBLE  
BONDS AND WHICH ARE BASED ON  
LINEAR DIISOCYANATES, AND THEIR  
USE

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows:

IN THE CLAIMS

Please amend the claims as shown in the marked-up copy following this amendment to read as follows:

1. (Amended) A polymerizable solid aliphatic polyurethane containing one or more olefinically unsaturated double bonds, said polyurethane having a very narrow melting range within the temperature range from 40 to 200°C, said polyurethane derived from
  - A) at least one linear aliphatic diisocyanate,

B) at least one aliphatic compound containing at least two isocyanate-reactive functional groups and/or water, and

C) at least one olefinically unsaturated compound containing an isocyanate-reactive functional group.

2. (Amended) The aliphatic polyurethane of claim 1, wherein the polyurethane has a melting range from 0.5 to 10°C.

3. (Amended) The aliphatic polyurethane of claim 1, wherein the polyurethane has a sharp melting point.

4. (Amended) The aliphatic polyurethane of claim 1, wherein the polyurethane has a very narrow melting range or a sharp melting point in the temperature range from 60 to 185°C.

5. (Amended) The aliphatic polyurethane of claim 1, wherein the polyurethane contains terminal and/or lateral olefinically unsaturated double bonds.

6. (Amended) The aliphatic polyurethane of claim 5, wherein the olefinically unsaturated double bonds are present in (meth)acrylate, vinyl ether, vinyl ester, allyl, allyl ether and/or allyl ester groups.

7. (Amended) The aliphatic polyurethane of claim 1, wherein the linear aliphatic diisocyanate A) represents a monomeric diisocyanate, an oligomeric diisocyanate, a polymeric diisocyanate or mixtures thereof, derived from

A) at least one linear aliphatic diisocyanate and

B) at least one aliphatic compound containing at least two isocyanate-reactive functional groups.

8. (Amended) The aliphatic polyurethane of claim 1, wherein the isocyanate-reactive functional groups are amino groups, thiol groups or hydroxyl groups.

9. (Amended) The aliphatic polyurethane of claim 8, wherein the aliphatic compound B) is linear.

10. (Amended) The aliphatic polyurethane of claim 9, wherein the linear aliphatic compound B) is a diamine, triamine, amino alcohol containing at least one amino group and at least one hydroxyl group, diol, triol, tetrol, sugar alcohol or mixtures thereof.

11. (Amended) The aliphatic polyurethane of claim 10, wherein the linear aliphatic compound B) is a low molecular weight diol, triol, a tetrol, a sugar alcohol having a molecular weight of from 62 to 200 daltons, a linear aliphatic oligomeric polyesterdiol, polymeric polyesterdiol, or polyetherdiol.

12. (Amended) The aliphatic polyurethane of claim 1, wherein

- (1) at least one diisocyanate A) is reacted with at least one compound C) in a molar ratio A):C) of 1:1 to give an adduct A/C) containing one isocyanate group and one olefinically unsaturated group, and then
- (2) the adduct A/C) is reacted with at least one compound B) in a molar ratio A/C):B) of x:1, wherein x is the number of the isocyanate-reactive groups in the at least one compound B), to give the aliphatic polyurethane.

13. (Amended) The aliphatic polyurethane of claim 1, wherein

- (1) at least one diisocyanate A) is reacted with at least one compound B) in a molar ratio A):B) of x:1, wherein x is the number of the isocyanate-reactive groups in the at least one compound B) to give the adduct A/B) containing x isocyanate groups, and then



(2) the adduct A/B) is reacted with at least one compound C) in a molar ratio C):A/B) of x:1, wherein x is the number of the isocyanate groups in the adduct A/B) to give the aliphatic polyurethane.

14. (Amended) The aliphatic polyurethane of claim 12 wherein x is a number from 2 to 6.

15. (Amended) The aliphatic polyurethane of claim 1, wherein the soft phase has a glass transition temperature  $T_g < 25^\circ\text{C}$ .

17. (Amended) A powder coating material curable thermally and/or curable with actinic radiation which comprises at least one aliphatic polyurethane according to claim 1.

18. (Amended) The powder coating material of claim 17, further comprising oligomers and/or polymers which are curable thermally and/or with actinic radiation and have a glass transition temperature  $T_g$  of more than  $40^\circ\text{C}$ .

19. (Amended) The powder coating material of claim 17 further comprising one or more customary coatings additives.

20. (Amended) The powder coating material of claim 17, wherein the powder coating material is in the form of a powder slurry coating material.

21. (Amended) A coating derived from a powder coating material according to claim 17.

22. (Amended) Primed and unprimed substrates comprising at least one coating according to claim 20.

Please add the following new claims.

23. (New) The aliphatic polyurethane of claim 1, wherein the polyurethane has a melting range of from 1 to 6°C.

24. (New) The aliphatic polyurethane of claim 6 wherein, the olefinically unsaturated double bonds are present in methacrylate groups, acrylate groups or mixtures thereof.

25. (New) The aliphatic polyurethane of claim 6, wherein the olefinically unsaturated double bonds are present in acrylate groups.

26. (New) The aliphatic polyurethane of claim 5, wherein the olefinically unsaturated double bonds are terminal.

27. (New) The aliphatic polyurethane of claim 1, wherein the isocyanate-reactive functional groups are amino groups, hydroxyl groups, or mixtures thereof.

28. (New) The aliphatic polyurethane of claim 1, wherein the isocyanate-reactive functional groups are hydroxyl groups.

29. (New) The aliphatic polyurethane of claim 12, wherein x is a whole number.

30. (New) The primed and unprimed substrates of claim 22, wherein the substrates are bodies of automobiles, bodies of commercial vehicles, industrial components, plastic parts, packaging, coils, electrical components, or furniture.


31. (New) A method for preparing powder coating materials, said method comprising mixing the aliphatic polyurethane according to claim 1 with a coating material to form a powder coating material.

REMARKS

Claims 1-15 and 17-31 are active in the present application. Claims 1-15 and 17-22 have been amended to remove multiple dependencies and for clarity. Claims 23-31 are new claims. Support for the new claims is found in the original claims. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



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**Marked-Up Copy**

Serial No: 10/088,530

Amendment Filed on:

8-15-2002

IN THE CLAIMS

--1. (Amended) A polymerizable solid aliphatic polyurethane containing one or more olefinically unsaturated double bonds, said polyurethane having a very narrow melting range within the temperature range from 40 to 200°C, [which is preparable] said polyurethane derived from

- A) at least one linear aliphatic diisocyanate,
- B) at least one aliphatic compound containing at least two isocyanate-reactive functional groups and/or water, and
- C) at least one olefinically unsaturated compound containing an isocyanate-reactive functional group.

2. (Amended) The aliphatic polyurethane of claim 1, [characterized in that it] wherein the polyurethane has a melting range from 0.5 to 10°C[, in particular from 1 to 6°C].

3. (Amended) The aliphatic polyurethane of claim 1 [or 2], [characterized in that it] wherein the polyurethane has a sharp melting point.

4. (Amended) The aliphatic polyurethane of [one of claims 1 to 3, characterized in that it] claim 1, wherein the polyurethane has a very narrow melting range or a sharp melting point in the temperature range from 60 to 185°C.

5. (Amended) The aliphatic polyurethane of [one of claims 1 to 4, characterized in that it] claim 1, wherein the polyurethane contains terminal and/or lateral[, especially terminal,] olefinically unsaturated double bonds.

6. (Amended) The aliphatic polyurethane of claim 5, [characterized in that] wherein the olefinically unsaturated double bonds are present in (meth)acrylate, vinyl ether, vinyl ester, allyl, allyl ether and/or allyl ester groups[, preferably methacrylate and/or acrylate groups, especially acrylate groups].

7. (Amended) The aliphatic polyurethane of [one of claims 1 to 6, characterized in that] claim 1, wherein the linear aliphatic diisocyanate A) represents a monomeric diisocyanate, [and/or] an oligomeric diisocyanate, [or] a polymeric diisocyanate or mixtures thereof, derived [preparable] from

- A) at least one linear aliphatic diisocyanate and
- B) at least one aliphatic compound containing at least two isocyanate-reactive functional groups.

8. (Amended) The aliphatic polyurethane of [one of claims 1 to 7, characterized in that] claim 1, wherein the isocyanate-reactive functional groups are amino groups, thiol groups [and/or] or hydroxyl groups[, preferably amino groups and/or hydroxyl groups, particularly hydroxyl groups].

9. (Amended) The aliphatic polyurethane of claim 8, [characterized in that] wherein the aliphatic compound B) is linear.

10. (Amended) The aliphatic polyurethane of claim 9, [that] wherein the linear aliphatic compound B) is a diamine, triamine, amino alcohol containing at least one amino group and at least one hydroxyl group, diol, triol, tetrol [and/or], sugar alcohol or mixtures thereof.

11. (Amended) The aliphatic polyurethane of claim 10, [characterized in that] wherein the linear aliphatic compound B) is a low molecular weight diol, triol, [or] a tetrol, [or] a sugar alcohol having a molecular weight of from 62 to 200 daltons, [and/or] a linear aliphatic oligomeric polyesterdiol, [and/or] polymeric polyesterdiol, or [and/or] polyetherdiol [is used as linear aliphatic compound B)].

12. (Amended) The aliphatic polyurethane of [one of claims 1 to 11, characterized in that] claim 1, wherein

- (1) at least one diisocyanate A) is reacted with at least one compound C) in a molar ratio A):C) of 1:1 to give an adduct A/C) containing one isocyanate group and one olefinically unsaturated group, and then
- (2) the adduct A/C) is reacted with at least one compound B) in a molar ratio A/C):B) of x:1, wherein x is the number of the isocyanate-reactive groups in the at least one compound B), to give the aliphatic polyurethane.

13. (Amended) The aliphatic polyurethane of [one of claims 1 to 11, characterized in that] claim 1, wherein

- (1) at least one diisocyanate A) is reacted with at least one compound B) in a molar ratio A):B) of x:1, wherein x is the number of the isocyanate-reactive groups in the at least one compound B) to give the adduct A/B) containing x isocyanate groups, and then
- (2) the adduct A/B) is reacted with at least one compound C) in a molar ratio C):A/B) of x:1, wherein x is the number of the isocyanate groups in the adduct A/B) to give the aliphatic polyurethane.

14. (Amended) The aliphatic polyurethane of claim 12 [or 13, characterized in that] wherein x is a number[, in particular a whole number,] from 2 to 6.

15. (Amended) The aliphatic polyurethane of [one of claims 1 to 14, characterized in that its] claim 1, wherein the soft phase has a glass transition temperature  $T_g < 25^\circ\text{C}$ .

17. (Amended) A powder coating material curable thermally and/or curable with actinic radiation which comprises [or consists of] at least one aliphatic polyurethane according to [one of claims 1 to 15] claim 1.

18. (Amended) The powder coating material of claim 17, [characterized in that it further comprises] further comprising oligomers and/or polymers which are curable thermally and/or with actinic radiation and have a glass transition temperature  $T_g$  of more than  $40^\circ\text{C}$ .

19. (Amended) The powder coating material of claim 17 [or 18, characterized in that it further comprises] further comprising one or more customary coatings additives.

20. (Amended) The powder coating material of [one of claims 17 to 19, characterized in that it] claim 17, wherein the powder coating material is in the form of a powder slurry coating material.

[illegible]

21. (Amended) A coating [producible] derived from a powder coating material according to [one of claims 17 to 20] claim 17.

22. (Amended) Primed and unprimed substrates[, especially bodies of automobiles and commercial vehicles, industrial components, including plastics parts, packaging, coils, and electrical components, or furniture,] comprising at least one coating according to claim 20.

Claims 23-31 (New).--



BASF/NAE 1036/99 PCT  
BASF Aktiengesellschaft

26.09.2000

Polymerizable solid aliphatic polyurethanes containing  
olefinically unsaturated double bonds and based on  
linear diisocyanates and use thereof

5 The present invention relates to novel polymerizable  
solid aliphatic polyurethanes containing olefinically  
unsaturated double bonds and based on linear  
diisocyanates. The present invention also relates to  
10 the use of the novel aliphatic polyurethanes as novel  
powder coating materials or for preparing novel powder  
coating materials. The present invention relates not  
least to the use of the novel powder coating materials  
for producing coatings on primed or unprimed  
substrates.

15

German patent application DE-A-24 36 186 discloses a  
polyurethane prepared from tolylene diisocyanate, an  
aromatic nonlinear diisocyanate, 2-hydroxyethyl  
methacrylate, and trimethylolpropane in a molar ratio  
20 of 3 : 3 : 1. The polyurethane has a melting point of  
approximately 65°C and a polymerizable double bond  
content of 2.9 double bonds per 1000 molecular weight.  
It can be used per se as a powder coating material  
curable with actinic radiation. Owing to the presence  
25 of aromatic structures, the coatings produced from it  
are not stable to weathering but instead tend to yellow  
under the effect of sunlight.

European patent application EP-A-0 410 242 discloses  
30 polyurethanes containing (meth)acryloyl groups in an  
amount corresponding to from 3 to 10% by weight, based  
on the polyurethane, of =C=C= (molecular weight 24).  
These known polyurethanes have unspecified melting  
points or melting ranges in the temperature range from  
35 50 to 180°C. They are prepared using isophorone  
diisocyanate, 4,4'-diisocyanatodicyclohexylmethane,  
4,4'-diisocyanatodiphenylmethane, its technical-grade

- 2 -

It is an object of the present invention to find novel  
20 polymerizable solid polyurethanes, containing  
olefinically unsaturated double bonds, which no longer  
have the disadvantages of the prior art but instead  
possess a very narrow melting range within the  
temperature range 40 to 200°C and can be used as powder  
25 coating materials or for preparing powder coating  
materials which give weathering-stable and nonyellowing  
coatings.

35 A) at least one linear aliphatic diisocyanate,

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- 3 -

- B) at least one aliphatic compound containing at least two isocyanate-reactive functional groups and/or water, and
- 5 C) at least one olefinically unsaturated compound containing an isocyanate-reactive functional group.

The novel polymerizable solid aliphatic polyurethane  
10 containing olefinically unsaturated double bonds is  
referred to below as "polyurethane of the invention".

Also found has been the novel powder coating material curable thermally and/or with actinic radiation which comprises or consists of at least one polyurethane of the invention and is referred to below as "powder coating material of the invention".

Found in addition have been novel coatings for primed  
20 or unprimed substrates that are produced from the  
powder coating material of the invention and are  
referred to below as "coatings of the invention".

Found not least have been primed or unprimed substrates  
25 which have at least one coating of the invention and  
are referred to below as "substrates of the invention".

Further subject matter of the invention will emerge from the description hereinbelow.

30 In the light of the prior art it was surprising and unforeseeable for the skilled worker that the object on which the present invention is based could be achieved by means of the polyurethanes of the invention. In particular it was surprising that the polyurethanes of 35 the invention have very narrow melting ranges or even sharp melting points and are therefore especially

The olefinically unsaturated double bonds may be present in any of a very wide variety of organic groups. What is essential is that the olefinically unsaturated double bonds are sufficiently reactive to be polymerizable. Examples of suitable organic groups containing olefinically unsaturated double bonds are (meth)acrylate, vinyl ether, vinyl ester, allyl, allyl ether and/or allyl ester groups, preferably methacrylate and/or acrylate groups. Of these, the



1,5-diethylcyclooctane, especially 1,4-dimethylcyclohexane.

Examples of especially suitable diisocyanates A) are  
5 tetramethylene 1,4-diisocyanate, hexamethylene 1,6-  
diisocyanate, octane-1,8-diyl diisocyanate, decane-  
1,10-diyl diisocyanate, dodecane-1,12-diyl diiso-  
cyanate, tetradecane-1,14-diyl diisocyanate, cyclo-  
hexane-1,4-diyl diisocyanate or 1,4-bis(isocyanato-  
10 methyl)cyclohexane.

Further examples of especially suitable diisocyanates  
A) are linear oligomeric or polymeric diisocyanates A)  
which are obtainable by the reaction of at least one of  
15 the above-described monomeric diisocyanates A) with at  
least one of the compound B) described below containing  
at least two isocyanate-reactive functional groups. In  
this case the molar proportions are chosen, as is  
known, in such a way as to give urethane prepolymers  
20 terminated by isocyanate groups.

In the context of the present invention, oligomeric  
diisocyanates A) are urethane prepolymers which contain  
in their molecule at least 2 to 15 repeating monomer  
25 units. In the context of the present invention,  
polymeric diisocyanates A) are urethane prepolymers  
which contain in their molecule at least 10 repeating  
monomer units. For further details of these terms,  
refer to Römpp Lexikon Lacke und Druckfarben, Georg  
30 Thieme Verlag, Stuttgart, New York, 1998, "oligomers",  
page 425.

The further essential starting product for the  
preparation of the polyurethanes of the invention is at  
35 least one aliphatic compound B) containing at least two  
isocyanate-reactive functional groups.

Instead of this compound B) or in addition thereto it is also possible to use water, which, as is known, reacts with two isocyanate groups to form a urea group, with the elimination of carbon dioxide.

The compound B) is linear or branched.

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Examples of suitable diamines B) are ethylenediamine, trimethylenediamine, tetramethylenediamine or hexamethylenediamine.

5 Examples of suitable triamines B) are diethylene-  
triamine or ethylenepropylenetriamine.

The diamines and triamines B) are preferably not used as the sole compounds B) but rather in combination with the amino alcohols and polyols B).

Examples of suitable amino alcohols B) containing two amino groups and one hydroxyl group are 2-hydroxytrimethylenediamine or 2-hydroxytetramethylenediamine.

15 Examples of suitable amino alcohols B) containing one amino group and two hydroxyl groups are diethanolamine or dipropanolamine.

20 Examples of suitable amino alcohols B) containing one tertiary amino group and three hydroxyl groups are triethanolamine or tripropanolamine.

Examples of suitable amino alcohols B) containing one  
25 amino group and one hydroxyl group are ethanolamine or  
propanolamine.

Examples of suitable unbranched diols B) are low molecular weight diols such as ethylene glycol, propylene glycol, 1,3-propanediol, butylene glycol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, diethylene glycol, dipropylene glycol or dibutylene glycol.

35 Examples of suitable oligomeric or polymeric diols B) are triethylene glycol, polyethylene glycol, polypropylene glycol, poly(co-ethylene-co-propylene glycol)



or tetrahydrofuran with a number-average molecular weight of more than 500 daltons, especially those having a narrow molecular weight distribution, which are also referred to as polyetherdiols.

5

Further examples of suitable oligomeric or polymeric diols B) are linear aliphatic polyesterpolyols.

As is known, linear aliphatic polyesterpolyols B) are  
10 obtainable by reacting linear aliphatic dicarboxylic acids and, if desired, tricarboxylic or tetracarboxylic acids and monocarboxylic acids in minor amounts or the esterifiable derivatives of these carboxylic acids, such as the anhydrides - where they exist - or the  
15 methyl, ethyl, propyl or butyl esters, with diols. In the context of the present invention, minor amounts are amounts which first cause no gelling of the polyesters (tricarboxylic or tetracarboxylic acids) and secondly do not terminate the polycondensation too early  
20 (monocarboxylic acids).

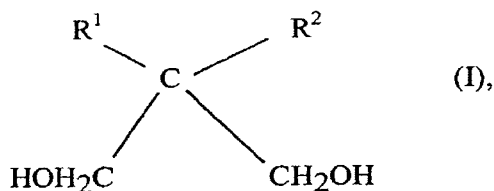
Examples of suitable linear aliphatic dicarboxylic acids are 1,3-cyclobutanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, malonic acid, succinic acid,  
25 glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedicarboxylic acid or dodecanedicarboxylic acid.

Examples of suitable tricarboxylic acids or tetra-  
30 carboxylic acids are 1,2,4-cyclohexanetricarboxylic acid or 1,2,4,5-cyclohexanetetracarboxylic acid.

Examples of suitable monocarboxylic acids are caproic acid, caprylic acid, capric acid, lauric acid, palmitic  
35 acid or stearic acid.

Examples of suitable linear aliphatic diols for preparing the linear polyesterdiols B) are the above-described diols B).

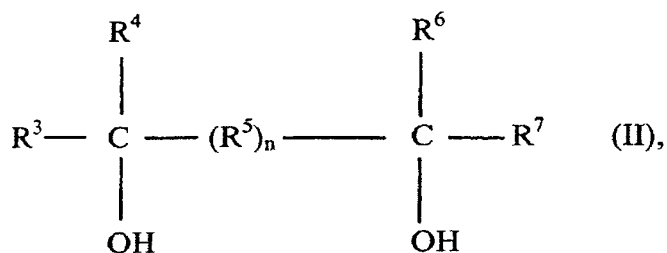
- 5 Examples of suitable branched aliphatic diols for preparing the linear polyesterdiols B) are neopentyl glycol, the positionally isomeric diethyloctanediols or diols of the formula I or II:



10

in which  $R^1$  and  $R^2$  each denote an identical or different radical and stand for an alkyl radical having from 1 to 18 carbon atoms or a cycloaliphatic radical, with the proviso that  $R^1$  and/or  $R^2$  must not be methyl;

15



20

in which  $R^3$ ,  $R^4$ ,  $R^6$  and  $R^7$  each denote identical or different radicals and stand for an alkyl radical having from 1 to 6 carbon atoms or cycloalkyl radical and  $R^5$  denotes an alkyl radical having from 1 to 6 carbon atoms, an aryl radical or an unsaturated alkyl radical having from 1 to 6 carbon atoms, and  $n$  is either 0 or 1.

25

Suitable diols I of the general formula I are all propanediols of the formula in which either  $R^1$  or  $R^2$  or

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R<sup>1</sup> and R<sup>2</sup> is not methyl, such as, for example, 2-butyl-2-ethylpropane-1,3-diol, 2-butyl-2-methylpropane-1,3-diol, 2-propyl-2-ethylpropane-1,3-diol, 2-di-tert-butylpropane-1,3-diol, 2-butyl-2-propylpropane-1,3-diol, 1-dihydroxymethylbicyclo[2.2.1]heptane, 2,2-diethylpropane-1,3-diol, 2,2-dipropylpropane-1,3-diol or 2-cyclohexyl-2-methylpropane-1,3-diol.

As diols II of the general formula II it is possible for example to use 2,5-dimethylhexane-2,5-diol, 2,5-diethylhexane-2,5-diol, 2-ethyl-5-methylhexane-2,5-diol or 2,4-dimethylpentane-2,4-diol.

The branched aliphatic diols may also be used per se as diols B). In both utilities they are advantageously used not as the sole diols but instead in a mixture with linear aliphatic compounds B). In that case the latter are preferably present in excess, i.e., at more than 50 mol%, in the mixture of compounds B).

The preparation of the linear aliphatic polyesterdiols B) has no special features in terms of its method but instead takes place in accordance with the customary and known methods of polyester chemistry, preferably in the presence of small amounts of a suitable solvent as azeotrope former. Examples of azeotrope formers used include aromatic hydrocarbons, such as xylene in particular, and (cyclo)aliphatic hydrocarbons, e.g., cyclohexane or methylcyclohexane.

Further examples of suitable oligomeric or polymeric linear aliphatic polyesterdiols B) are polyesterdiols obtained by reacting a lactone with a diol. They are distinguished by the presence of terminal hydroxyl groups and repeating polyester fractions of the formula  $-(-CO-(CHR^8)_m-CH_2-O)-$ . In this formula the index m is preferably from 4 to 6 and the substituent R<sup>8</sup> =

hydrogen or an alkyl, cycloalkyl or alkoxy radical. No substituent contains more than 12 carbon atoms. The total number of carbon atoms in the substituent does not exceed 12 per lactone ring. Examples thereof are

5 hydroxycaproic acid, hydroxybutyric acid, hydroxy-decanoic acid and/or hydroxystearic acid.

For preparing the polyesterdiols B) of this kind preference is given to the unsubstituted ###-caprolactone, in which m has the value 4 and all R<sup>8</sup> substituents are hydrogen. The reaction with lactone is initiated by low molecular weight polyols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol or dimethylolcyclohexane. It is, however, also possible to

15 react other reaction components, such as ethylenediamine, alkyldialkanolamines or else urea, with caprolactone. Other suitable diols of relatively high molecular weight include polylactamdiols, which are prepared by reacting, for example, ###-caprolactam

20 with low molecular weight diols.

Examples of highly suitable linear aliphatic polyesterdiols B) of the type described above are the polycaprolactonediolis sold under the brand name CAPA®

25 by Solvay Interlox.

Examples of suitable triols B) are trimethylolethane, trimethylolpropane or glycerol, especially trimethylolpropane.

30

Examples of suitable tetrols B) are pentaerythritol or homopentaerythritol.

Examples of suitable higher polyfunctional polyols B)

35 are sugar alcohols such as threitol, erythritol, arabitol, adonitol, xylitol, sorbitol, mannitol or dulcitol.

All of the compounds B) described above may be used, as already mentioned above, for preparing the oligomeric and polymeric diisocyanates A).

5

In accordance with the invention it is of advantage to select the compounds A) and the compounds B) so as to give polyurethanes of the invention whose soft phase has a glass transition temperature  $T_g < 25^\circ\text{C}$ .

10

The third inventively essential starting product for preparing the polyurethanes of the invention is at least one olefinically unsaturated compound C) containing an isocyanate-reactive functional group.

15

Although in accordance with the invention it is also possible to employ aromatic compounds containing at least one group having at least one olefinically unsaturated double bond, such as styrene derivatives, for example, as compounds C), it is nevertheless of advantage in accordance with the invention if the compounds C) contain no aromatic groups.

20

Examples of suitable isocyanate-reactive functional groups are those described above, particularly the hydroxyl group.

25

Examples of suitable olefinically unsaturated groups are (meth)acrylate, vinyl ether, vinyl ester, allyl, allyl ether and/or allyl ester groups, preferably methacrylate, acrylate and/or allyl groups, but especially acrylate groups.

30

The compound C) for use in accordance with the invention contains one olefinically unsaturated double bond or two or three olefinically unsaturated double bonds. In specific cases it may also contain more than

35

three olefinically unsaturated double bonds. Of advantage in accordance with the invention is one olefinically unsaturated double bond.

5 Examples of highly suitable compounds C) for use in accordance with the invention are, accordingly, customary and known monomers which carry per molecule at least one hydroxyl group, such as

10 - allyl alcohol;

- hydroxyalkyl esters of acrylic acid or of  
methacrylic acid, especially of acrylic acid,  
which are obtainable by esterifying aliphatic  
15 diols, the above-described low molecular mass  
diols B) for example, with acrylic acid or  
methacrylic acid or by reacting acrylic acid or  
methacrylic acid with an alkylene oxide;  
especially hydroxyalkyl esters of acrylic acid or  
20 methacrylic acid in which the hydroxyalkyl group  
contains up to 20 carbon atoms, such as 2-  
hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-  
hydroxybutyl, 4-hydroxybutyl or bis(hydroxy-  
methyl)cyclohexane acrylate or methacrylate; or

25 - reaction products of cyclic esters, such as  
epsilon-caprolactone, and these hydroxyalkyl or  
hydroxycycloalkyl esters.

30 The polyurethanes of the invention are advantageously  
prepared by

(1) reacting at least one diisocyanate A) with at  
least one compound C) in a molar ratio A) : C) of  
35 1 : 1 to give an adduct A/C) containing one  
isocyanate group and one olefinically unsaturated  
group, and then

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(2) reacting the adduct A/C) with at least one compound B) in a molar ratio A/C) : B) of  $x : 1$ , wherein  $x$  is the number of the isocyanate-reactive groups in the at least one compound B), to give the polyurethanes of the invention.

According to another advantageous variant, the polyurethanes of the invention are prepared by

10 (1) reacting at least one diisocyanate A) with at  
least one compound B) in a molar ratio A) : B) of  
x : 1, wherein x is the number of the isocyanate-  
reactive groups in the at least one compound B) to  
give the adduct A/B) containing x isocyanate  
15 groups, and then

(2) reacting the adduct A/B) with at least one compound C) in a molar ratio C) : A/B) of  $x : 1$ , wherein  $x$  is the number of the isocyanate groups in the adduct A/B) to give the aliphatic polyurethanes.

In accordance with the invention it is of advantage if x is a number, in particular a whole number, from 2 to 25 6, preferably 2 to 5, with particular preference 2 to 4, with very particular preference 2 and 3, and in particular 2.

Viewed in terms of their methods, the processes have no special features but instead take place in accordance with the customary and known methods of organic isocyanate chemistry. The reactions are preferably conducted under inert gas using temperatures from 20 to 120°C, preferably from 30 to 100°C, more preferably from 40 to 80°C, and particularly from 50 to 70°C. In general it is advisable to conduct the reactions in an organic solvent or solvent mixture that is not





acrylated polyesters, polylactones, polycarbonates, polyethers, epoxy resin-amine adducts, (meth)acrylate-diols, partially hydrolyzed polyvinyl esters or polyureas which are curable thermally and/or with actinic radiation, or (meth)acryloyl-functional (meth)-acrylate copolymers, polyether acrylates, polyester acrylates, unsaturated polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, silicone acrylates, and the corresponding methacrylates, which are curable with actinic radiation.

Examples of especially suitable oligomers or polymers which can be used as further ingredients in the powder coating materials of the invention are the crosslinkable copolymers such as are described in European patents EP-A-0 650 985, EP-A-0 650 978 or EP-A-0 650 979.

Furthermore, the powder coating materials of the invention may comprise customary coatings additives. Examples of suitable customary coatings additives for use in the powder coating materials of the invention are

- customary and known reactive diluents curable thermally and/or with actinic radiation, such as positionally isomeric diethyloctanediols or hydroxyl-containing hyperbranched compounds or dendrimers, (meth)acrylates with a functionality of two or more, or polyisocyanates containing (meth)acrylate groups;
- other crosslinking agents such as amino resins, compounds or resins containing anhydride groups, compounds or resins containing epoxide groups, tris(alkoxycarbonylamino)triazines, compounds or

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resins containing carbonate groups, blocked and/or nonblocked polyisocyanates, beta-hydroxyalkyl-amides, and compounds containing on average at least two groups capable of transesterification, examples being reaction products of malonic diesters and polyisocyanates or of esters and partial esters of polyhydric alcohols of malonic acid with monoisocyanates, such as are described in European patent EP-A-0 596 460;

- UV absorbers;

- light stabilizers such as HALS compounds, benzotriazoles or oxalanilides;

- free radical scavengers;

- thermolabile free-radical initiators such as organic peroxides, organic azo compounds or C-C-cleaving initiators such as dialkyl peroxides, peroxocarboxylic acids, peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azodinitriles or benzpinacol silyl ethers;

- crosslinking catalysts such as dibutyl tin dilaurate, lithium decanoate or zinc octoate;

- devolatilizers such as diazadicycloundecane or benzoin;

- photoinitiators such as those of the Norrish II type, whose mechanism of action is based on an intramolecular variant of the hydrogen abstraction reactions such as occur diversely in photochemical reactions (by way of example, reference may be made here to Römpp Chemie Lexikon, 9th expanded and revised edition, Georg Thieme Verlag

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- Stuttgart, vol. 4, 1991) or cationic photo-initiators (by way of example, reference may be made here to Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag Stuttgart, 1998, pages 444 to 446), especially benzophenones, benzoin ethers or phosphine oxides;
- slip additives;
  - 10 - polymerization inhibitors;
  - adhesion promoters such as tricyclodecane-dimethanol;
  - 15 - leveling agents;
  - transparent fillers based on silicon dioxide, aluminum oxide, titanium dioxide or zirconium oxide; for further details refer to Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, 1998, pages 250 to 252;
  - 20 - flame retardants;
  - 25 - flatting agents such as magnesium stearate;
  - electrically conductive pigments, such as metal pigments, conductivity blacks, doped pearlescent pigments or conductive barium sulfate. Especially suitable electrically conductive pigments are the conductivity blacks; for further details refer to Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, New York, 1998, "metal pigments", p. 381, and "conductive pigments", p. 354;
  - 30
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These additives are added to the powder coating materials of the invention in customary and known, effective amounts, which depending on additive may be from 0.001 to 500 parts by weight per 100 parts by weight of polyurethane of the invention.

The preparation of the powder coating materials of the invention has no special features as far as its method is concerned but instead takes place in a customary and known manner, preferably by mixing of the ingredients in the melt, by extrusion or kneading, discharging the melt from the mixing unit, solidifying the resulting homogenized mass, comminuting the mass until the desired particle size results, and, where appropriate, sieving the resulting powder coating material of the invention under conditions under which there is no premature thermal crosslinking and/or crosslinking with actinic radiation and/or other damage to individual ingredients of the powder coating material of the invention, as a result, for example, of thermal degradation.

In this context it proves a further particular advantage of the powder coating material of the invention that it can be dispersed in water to give a powder slurry coating material of the invention.

The application of the powder coating material of the invention also has no special features as far as its method is concerned but instead takes place by means of customary and known techniques and apparatus, by electrostatic spraying, for example, for which again conditions are employed under which there is no premature thermal crosslinking and/or crosslinking with actinic radiation and/or other damage to individual ingredients of the powder coating material of the

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invention, as a result, for example, of thermal degradation.

The powder slurry coating material of the invention, on  
5 the other hand, can be applied by means of techniques  
and apparatus such as are commonly employed for the  
application of spray coating materials.

The powder coating material of the invention and the powder slurry coating material of the invention can be applied in any of a wide variety of film thicknesses to give coatings with any of a wide variety of thicknesses, in particular from 10 to 250  $\mu\text{m}$ . The thickness of the coatings is guided by the intended use of the coatings and can therefore be adjusted readily by the skilled worker.

The curing of the applied powder coating films also has no special features as far as its method is concerned; instead, the customary and known techniques and apparatus are employed.

Accordingly, curing with actinic radiation can be carried out using electromagnetic radiation such as X-rays, UV radiation, visible light or near IR (NIR) light or using corpuscular radiation such as electron beams. Techniques and apparatus for curing with actinic radiation are customary and known and are described, for example, in R. Holmes, "U.V. and E.B. Curing Formulations for Printing Inks", Coatings and Paints, SITA Technology, Academic Press, London, United Kingdom 1984.

Thermal curing likewise has no special features as far  
35 as its method is concerned but instead takes place in  
accordance with the customary and known methods such as

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heating in a forced air oven or irradiation using IR lamps.

Suitable substrates include all surfaces to be coated  
5 on articles that are amenable to curing of the coating  
films present thereon using heat and/or actinic  
radiation; examples are articles made of metals,  
plastics, wood, ceramic, stone, textile, fiber  
10 composites, leather, glass, glass fibers, glass wool  
and rock wool or mineral-bound and resin-bound building  
materials, such as plasterboard, cement slabs or  
roofing shingles. Accordingly, the powder coating  
material or powderslurry coating material of the  
invention, especially as a clearcoat material, is  
15 suitable for applications in automobile finishing, in  
the coating of furniture, and in industrial coating,  
including coil coating, container coating, and the  
coating of electrical components, to a high degree. In  
the context of the industrial coatings it is suitable  
20 for coating virtually all parts for private or  
industrial use such as radiators, domestic appliances,  
small metal parts, hubcaps, wheel rims or windings of  
electrical motors.

25 The clearcoat of the invention is particularly suitable  
as a coating over basecoat materials, preferably in the  
automobile industry. It is especially suitable as a  
clearcoat over aqueous basecoat materials based on  
polyesters, polyurethane resins, and amino resins.

30 The metallic substrates employed in this context may  
have a primer system, in particular a cathodically or  
anodically deposited and thermally cured electrocoat.  
Where appropriate, the electrocoat may also have been  
35 coated with an antistonechip primer or with a surfacer.

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With the powder coating and powderslurry coating material of the invention it is also possible in particular to coat primed or unprimed plastics such as, for example, ABS, AMMA, ASA, CA, CAB, EP, UF, CF, MF, MPF, PF, PAN, PA, PE, HDPE, LDPE, LLDPE, UHMWPE, PC, PET, PMMA, PP, PS, SB, PUR, PVC, RF, SAN, PBT, PPE, POM, PUR-RIM, SMC, BMC, PP-EPDM, and UP (abbreviations in accordance with DIN 7728T1). The plastics to be coated can of course also be polymer blends, modified plastics or fiber reinforced plastics. It is also possible to employ them for the coating of plastics commonly used in vehicle construction, especially motor vehicle construction.

15 In the case of nonfunctionalized and/or apolar substrate surfaces, these may be subjected prior to coating in the known manner to a pretreatment with a plasma or by flaming and/or may be coated with a hydroprimer system comprising a hydroprimer.

20

The coatings of the invention produced from the powder coating materials and powderslurry coating materials of the invention exhibit outstanding leveling and have an outstanding overall appearance. They are stable to weathering and do not yellow even in a tropical climate. They can therefore be used for numerous utilities inside and out. Accordingly, primed and unprimed substrates, especially bodies of automobiles and commercial vehicles, industrial components, including plastics parts, packaging, coils, and electrical components, or furniture that have been coated with at least one coating of the invention have particular technical and economic advantages, in particular a long surface life, which makes them particularly attractive for the users.



The preparation of the polyurethanes 1 to 16 of the invention

1680 parts by weight of hexamethylene diisocyanate and  
15 0.84 parts by weight of dibutyltin dilaurate (500 ppm  
based on hexamethylene diisocyanate) were charged under  
nitrogen to a suitable reaction vessel and heated to  
60°C. At this temperature, 116 parts by weight of  
hydroxyethyl acrylate were added dropwise over the  
20 course of 30 minutes. Thereafter the resulting reaction  
mixture was left to react at 60°C for 60 minutes.  
Subsequently the reaction mixture was freed from  
monomeric hexamethylene diisocyanate by distilling it  
on a thin film evaporator at an oil temperature of  
25 165°C under a pressure of 2.5 mbar. The resulting  
adduct was a viscous oil which slowly crystalized at  
room temperature. Its residual monomer content was  
below 0.2% by weight.

0.1 mol of a compound B) (cf. table 1) was dissolved in  
35 250 ml of methyl ethyl ketone. The equimolar amounts of  
the adducts described above, listed in table 1, were  
added to the resultant solution. Then 500 ppm, based on

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the adduct, of dibutyltin dilaurate were added and the resulting reaction mixture was heated to 60°C. It was stirred at this temperature for two hours more, then cooled and held in a refrigerator at 3°C for twelve hours. The solid precipitated was filtered off with suction, washed twice with 50 ml portions of methyl ethyl ketone, and dried in vacuo. The melting points of the polyurethanes 1 to 16 of the invention can be found in table 1.

10

**Table 1: Starting products and their molar ratios and also the melting ranges or melting points of the polyurethanes of the invention**

Example No.	Compound B) (°C)	Molar ratio melting range/B) : adduct A/C)	Melting point
1	Ethylene glycol	1 : 2	124
2	1,2-Propanediol	1 : 2	91
3	1,3-Propanediol	1 : 2	118
4	1,3-Butanediol	1 : 2	97 to 100
5	1,4-Butanediol	1 : 2	135
6	1,5-Pentanediol	1 : 2	125
7	1,6-Hexanediol	1 : 2	128
8	CAPA® 200	1 : 2	115
9	CAPA® 212	1 : 2	125 to 128
10	CAPA® 222	1 : 2	119 to 122
11	Ethanolamine	1 : 2	128 to 130
12	1,4-Cyclohexanediol	1 : 2	105 to 108
13	Glycerol	1 : 3	105 to 107
14	Mannitol	1 : 6	105 to 108
15	Trimethylolethane	1 : 3	117 to 118
16	Water	1 : 3	120 to 125

15

CAPA® = polycaprolactonediods from Solvay Interlox

The polyurethanes 1 to 16 of the invention were outstandingly suitable for preparing powder coating materials.

5   **Examples 17 to 21**

**The preparation of the polyurethanes 17 to 21 of the invention**

10   The polyurethanes 17 to 21 of the invention were prepared in accordance with the following general instructions:

0.1 mol of at least one compound B) (cf. table 2) was  
15   dissolved in 250 ml of methyl ethyl ketone. To the solution there were added, based on the amount of hexamethylene diisocyanate, 500 ppm of dibutyltin dilaurate, after which the resulting mixture was heated to 70°C. Subsequently the equimolar amount of  
20   hexamethylene diisocyanate, as listed in table 2, was added over the course of 10 minutes, after which the resulting reaction mixture was stirred at 70°C for one hour. Then the equimolar amount of hydroxyethyl acrylate, indicated in table 2, was added over ten  
25   minutes. The resulting reaction mixture was further stirred at 70°C for one hour, after which it was left to cool and held in a refrigerator at 3°C for twelve hours. The solid precipitated was filtered off with suction, washed twice with 50 ml portions of methyl  
30   ethyl ketone, and dried in vacuo. Table 2 gives an overview of the starting products, their molar ratios, and the melting ranges or melting points.

35   **Table 2: Starting products and their molar ratios and also the melting ranges or melting points of the polyurethanes of the invention**

Example No.	Compounds B)	Molar ratio B) : C) : A)	Melting interval/ melting point (°C)
17	1,4-Butanediol	1 : 2 : 2	161
18	CAPA® 222	1 : 2 : 2	120 to 122
19	CAPA® 212	(0.2 : 0.8) :	102
	Ethylene glycol	2 : 2	
20	Ethylene glycol	1 : 0.5 : 1.5	145 to 150
21	1,4-Cyclohexanediol	1 : 2 : 2	180 to 185

A) = hexamethylene diisocyanate;

C) = hydroxyethyl acrylate;

5 CAPA® = polycaprolactonediolis from Solvay Interlox

The polyurethanes 17 to 21 of the invention were outstandingly suitable for the preparation of powder coating materials.

## 5 Claims

A) at least one linear aliphatic diisocyanate,

C) at least one olefinically unsaturated compound  
20 containing an isocyanate-reactive functional  
group.

3. The aliphatic polyurethane of claim 1 or 2, characterized in that it has a sharp melting point.

35 5. The aliphatic polyurethane of one of claims 1 to  
4, characterized in that it contains terminal and/or

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lateral, especially terminal, olefinically unsaturated double bonds.

6. The aliphatic polyurethane of claim 5, characterized in that the olefinically unsaturated double bonds are present in (meth)acrylate, vinyl ether, vinyl ester, allyl, allyl ether and/or allyl ester groups, preferably methacrylate and/or acrylate groups, especially acrylate groups.

10

7. The aliphatic polyurethane of one of claims 1 to 6, characterized in that the linear aliphatic diisocyanate A) represents a monomeric diisocyanate and/or an oligomeric or polymeric diisocyanate preparable from

15

A) at least one linear aliphatic diisocyanate and

B) at least one aliphatic compound containing at least two isocyanate-reactive functional groups.

20

8. The aliphatic polyurethane of one of claims 1 to 7, characterized in that the isocyanate-reactive functional groups are amino groups, thiol groups and/or hydroxyl groups, preferably amino groups and/or hydroxyl groups, particularly hydroxyl groups.

25

9. The aliphatic polyurethane of claim 8, characterized in that the aliphatic compound B) is linear.

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10. The aliphatic polyurethane of claim 9, that the linear aliphatic compound B) is a diamine, triamine, amino alcohol containing at least one amino group and at least one hydroxyl group, diol, triol, tetrol and/or sugar alcohol.

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11. The aliphatic polyurethane of claim 10, characterized in that a low molecular weight diol, triol or a tetrol or a sugar alcohol having a molecular weight of from 62 to 200 daltons and/or a linear aliphatic oligomeric and/or polymeric polyesterdiol and/or polyetherdiol is used as linear aliphatic compound B).

(1) at least one diisocyanate A) is reacted with at least one compound C) in a molar ratio A) : C) of 1 : 1 to give an adduct A/C) containing one isocyanate group and one olefinically unsaturated group, and then

13. The aliphatic polyurethane of one of claims 1 to 11, characterized in that

(2) the adduct A/B) is reacted with at least one  
35 compound C) in a molar ratio C) : A/B) of  $x : 1$ ,  
wherein  $x$  is the number of the isocyanate groups

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in the adduct A/B) to give the aliphatic polyurethane.

14. The aliphatic polyurethane of claim 12 or 13,  
5 characterized in that x is a number, in particular a whole number, from 2 to 6.

15. The aliphatic polyurethane of one of claims 1 to 14, characterized in that its soft phase has a glass  
10 transition temperature  $T_g < 25^\circ\text{C}$ .

16. Use of the aliphatic polyurethane according to one of claims 1 to 15 as powder coating material or for preparing powder coating materials.

15 17. A powder coating material curable thermally and/or with actinic radiation which comprises or consists of at least one aliphatic polyurethane according to one of claims 1 to 15.

20 18. The powder coating material of claim 17, characterized in that it further comprises oligomers and/or polymers which are curable thermally and/or with actinic radiation and have a glass transition  
25 temperature  $T_g$  of more than  $40^\circ\text{C}$ .

19. The powder coating material of claim 17 or 18, characterized in that it further comprises customary coatings additives.

30 20. The powder coating material of one of claims 17 to 19, characterized in that it is in the form of a powder slurry coating material.

35 21. A coating producible from a powder coating material according to one of claims 17 to 20.



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**Polymerizable solid aliphatic polyurethanes containing olefinically unsaturated double bonds and based on linear diisocyanates and use thereof**

5 **Abstract**

A polymerizable solid aliphatic polyurethane containing olefinically unsaturated double bonds, having a very narrow melting range within the temperature range from  
10 40 to 200°C, which is preparable from

- A) at least one linear aliphatic diisocyanate,
- 15 B) at least one aliphatic compound containing at least two isocyanate-reactive functional groups and/or water, and
- 20 C) at least one olefinically unsaturated compound containing an isocyanate-reactive functional group,

and its use as a powder coating material or for preparing powder coating materials.

# Declaration, Power of Attorney

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We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"POLYMERISIERBARE OLEFINISCH UNGESÄTTIGTE DOPPELBINDUNGEN  
ENTHALTENDE FESTE ALIPHATISCHE POLYURETHANE AUF DER BASIS  
LINEARER DIISOCYANATE UND IHRE VERWENDUNG"

the specification of which

☐ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/EP00/09627

on OCT 2, 2000

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19947522.9	Germany	02 October 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

_____	_____
(Application Number)	(Filing Date)
_____	_____
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint: Norman F. Oblon, Registration Number 24, 618;  
Marvin J. Spivak, Registration Number 24, 913;  
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Stephen G. Baxter, Registration Number 32, 884;  
Richard L. Treanor, Registration Number 36, 379;  
Robert W. Hahl, Registration Number 33, 893;  
our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

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We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

**Declaration**

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